

2-Amino-5-methylpyridinium dibromiodate

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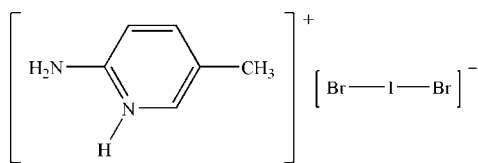
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.040; wR factor = 0.096; data-to-parameter ratio = 24.2.

In the title salt, $\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{Br}_2\text{I}^-$, the cation is essentially planar (r.m.s. deviation = 0.0062 Å for the non-H atoms) while the anion is almost linear with a $\text{Br}-\text{I}-\text{Br}$ angle of $177.67(2)^\circ$. The crystal packing shows two anions and two cations connected *via* $\text{N}-\text{H}\cdots\text{Br}$ and (pyridine) $\text{N}-\text{H}\cdots\text{Br}$ hydrogen-bonding interactions, forming centrosymmetric tetramers with $R_4^4(16)$ ring motifs. Very weak offset aromatic $\pi-\pi$ stacking interactions [centroid-centroid separation = 4.038 (4), slippage = 1.773 Å] also occur.

Related literature

For background to this study, see: Al-Far *et al.* (2012); Kochel (2006). For comparison bond lengths and angles, see: Gardberg *et al.* (2002); Hemamalini & Fun (2010). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{Br}_2\text{I}^-$

$M_r = 395.85$

Triclinic, $P\bar{1}$

$a = 8.3648(13)$ Å

$b = 8.4233(16)$ Å

$c = 9.2321(16)$ Å

$\alpha = 105.107(16)^\circ$

$\beta = 115.371(16)^\circ$

$\gamma = 98.241(15)^\circ$

$V = 542.7(2)$ Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 10.26$ mm⁻¹

$T = 293$ K

$0.54 \times 0.39 \times 0.30$ mm

Data collection

Agilent Xcalibur Eos diffractometer

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2011)

$T_{\min} = 0.011$, $T_{\max} = 0.045$

4283 measured reflections

2465 independent reflections

1777 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.096$

$S = 1.01$

2465 reflections

102 parameters

H-atom parameters constrained

$\Delta\rho_{\max} = 1.17$ e Å⁻³

$\Delta\rho_{\min} = -0.85$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{Br2}$	0.86	2.73	3.499 (5)	150
$\text{N2}-\text{H2B}\cdots\text{Br1}^i$	0.86	2.70	3.545 (6)	168

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The structure was determined at the Hamdi Mango Center for Scientific Research at the University of Jordan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2581).

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supplementary materials

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Comment

Polyhalides display a variety of structures. Various compounds with interesting structures were found when protonated aromatic nitrogen bases were combined with polyhalides (Kochel, 2006). Continuing our research in this area (Al-Far *et al.*, 2012), we now report the crystal structure of the title compound in this article. The crystals of the title compound were found as an unexpected product from a reaction mixture of CdI₂, HBr, 2-amino-5-methylpyridine and Br₂ upon attempting to synthesize [(C₇H₁₀N)]₂ [CdBr₄] complex of 2-amino-5-methylpyridinium.

In the title compound (Fig. 1), the cation, 2-amino-5-methylpyridinium, is essentially planar (r.m.s.d = 0.0062 Å). The IBr₂⁻ anion is symmetrical and almost linear, Br1—I—Br2 angle of 177.67 (2) °, with I—Br distances 2.6836 (10) and 2.7119 (10) Å. These values are in agreement with the values reported in the literature (Gardberg *et al.*, 2002). The molecular dimensions of the cation are also as expected (Hemamalini & Fun, 2010).

The crystal structure (Fig. 2), shows stacks of anions separated by layers of cations. The anions and cations are connected *via* H—N—H...Br and pyN—H...Br hydrogen bonding (Table 1), forming centrosymmetric tetramers (two cation and two anions). These tetramers form sixteen membered rings in graph set motif *R*₄⁴(16) (Bernstein *et al.*, 1995). The rings are further connected *via* π ... π interactions between the cations with separation between the ring centroids [*C*_g...*C*_g (2 - *x*, -*y*, 1 - *z*)] being 4.038 (4) Å. Both hydrogen bonding and π ... π interactions consolidate a three dimensional network.

Experimental

A solution of CdI₂ (0.37 g, 1.0 mmol) dissolved in 95% EtOH (10 ml) and 60% HBr (1 ml) solution was added to a mixture of 2-amino-5-methylpyridine (0.11 g, 1.0 mmol) dissolved in 95% EtOH (10 ml), 60% HBr (1 ml) and molecular bromine (2 ml). The resulting mixture was refluxed for 2.5 hr. On slow evaporation at room temperature yellow plates of the title compound were formed in 4 days (yield 85%).

Refinement

All H atoms were positioned geometrically and refined using a riding model, with N—H = 0.86 Å and C—H = 0.93 and 0.96 Å, for aryl and methyl H-atoms, respectively. The *U*_{iso}(H) were allowed at 1.5*U*_{eq}(C methyl) or 1.2*U*_{eq}(N/C non-methyl).

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO* (Agilent, 2011); data reduction: *CrysAlis PRO* (Agilent, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

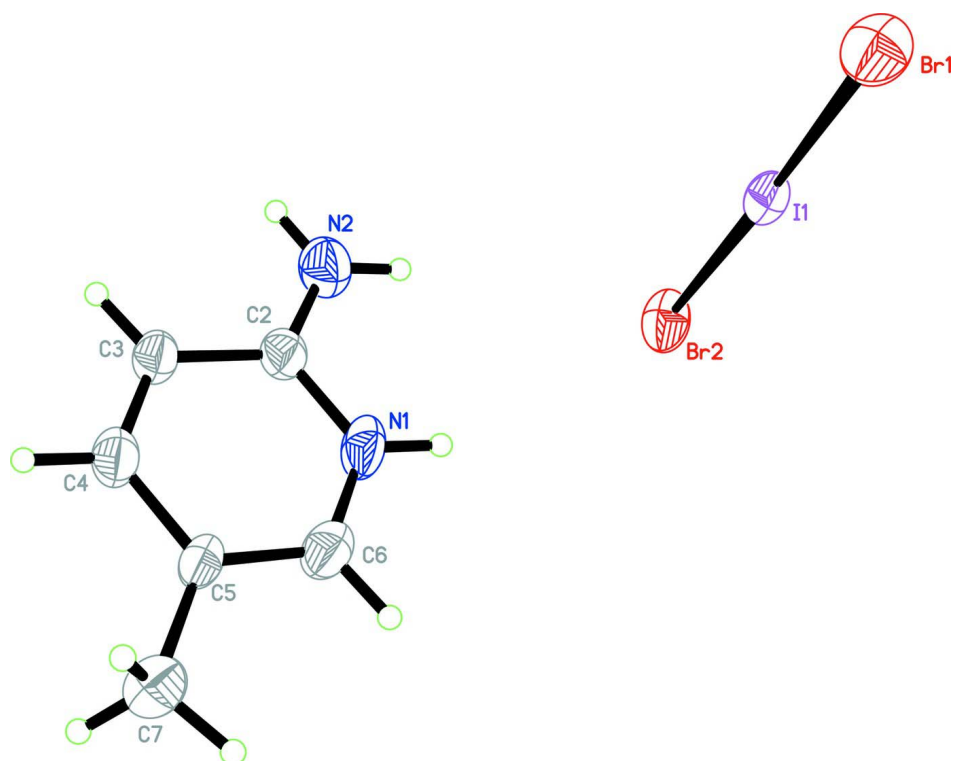
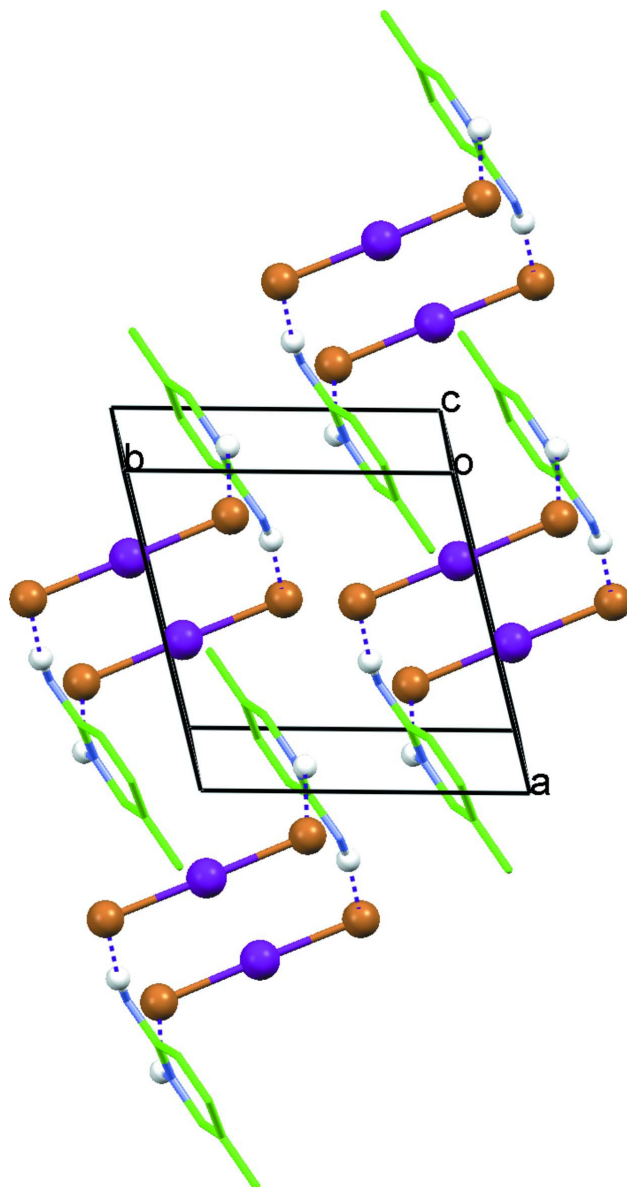


Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as small spheres of arbitrary radius.

**Figure 2**

A view of the $\text{pyN-H}\cdots\text{Br}$ and $\text{H-N-H}\cdots\text{Br}$ hydrogen bonds (dotted lines) in the crystal structure of the title compound. H atoms non-participating in hydrogen-bonding were omitted for clarity.

2-Amino-5-methylpyridinium dibromoiodate

Crystal data

$\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{Br}_2\text{I}^-$

$M_r = 395.85$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.3648\ (13)\ \text{\AA}$

$b = 8.4233\ (16)\ \text{\AA}$

$c = 9.2321\ (16)\ \text{\AA}$

$\alpha = 105.107\ (16)^\circ$

$\beta = 115.371\ (16)^\circ$

$\gamma = 98.241\ (15)^\circ$

$V = 542.7\ (2)\ \text{\AA}^3$

$Z = 2$

$F(000) = 364$

$D_x = 2.422\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1406 reflections

$\theta = 3.2\text{--}30.0^\circ$

$\mu = 10.26\ \text{mm}^{-1}$

$T = 293$ K
Plate, yellow

$0.54 \times 0.39 \times 0.30$ mm

Data collection

Agilent Xcalibur Eos
diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0534 pixels mm^{-1}
 ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2011)
 $T_{\min} = 0.011$, $T_{\max} = 0.045$

4283 measured reflections
2465 independent reflections
1777 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\max} = 29.1^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -11 \rightarrow 10$
 $k = -11 \rightarrow 11$
 $l = -10 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.096$
 $S = 1.01$
2465 reflections
102 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.035P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.85 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0292 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.0416 (7)	0.3049 (7)	0.7106 (6)	0.0606 (15)
H1A	1.0387	0.3331	0.8057	0.073*
I1	0.70649 (5)	-0.04784 (5)	0.90281 (5)	0.04214 (17)
Br1	0.55742 (10)	-0.38624 (9)	0.80942 (10)	0.0661 (2)
N2	0.7745 (7)	0.3836 (7)	0.5894 (7)	0.0699 (17)
H2A	0.7751	0.4121	0.6862	0.084*
H2B	0.6882	0.3947	0.5021	0.084*
C2	0.9069 (8)	0.3223 (8)	0.5748 (8)	0.0509 (16)
Br2	0.85761 (10)	0.29148 (9)	0.98508 (9)	0.0589 (2)
C3	0.9133 (8)	0.2686 (8)	0.4207 (8)	0.0500 (15)
H3A	0.8224	0.2749	0.3211	0.060*
C4	1.0533 (8)	0.2076 (9)	0.4194 (8)	0.0551 (17)

H4A	1.0562	0.1728	0.3166	0.066*
C5	1.1936 (8)	0.1936 (8)	0.5625 (7)	0.0438 (14)
C6	1.1819 (9)	0.2455 (9)	0.7061 (9)	0.0591 (18)
H6A	1.2732	0.2406	0.8064	0.071*
C7	1.3488 (8)	0.1264 (9)	0.5598 (9)	0.0647 (19)
H7A	1.4329	0.1335	0.6734	0.097*
H7B	1.4130	0.1938	0.5211	0.097*
H7C	1.2999	0.0087	0.4830	0.097*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.077 (4)	0.061 (4)	0.032 (3)	0.007 (3)	0.025 (3)	0.008 (3)
I1	0.0468 (3)	0.0479 (3)	0.0301 (2)	0.01598 (19)	0.01656 (19)	0.01427 (19)
Br1	0.0739 (5)	0.0464 (4)	0.0580 (5)	0.0088 (4)	0.0210 (4)	0.0132 (4)
N2	0.076 (4)	0.076 (5)	0.060 (4)	0.019 (3)	0.039 (3)	0.019 (4)
C2	0.052 (3)	0.050 (4)	0.046 (4)	0.002 (3)	0.023 (3)	0.018 (3)
Br2	0.0794 (5)	0.0461 (4)	0.0465 (4)	0.0117 (4)	0.0284 (4)	0.0173 (4)
C3	0.054 (4)	0.054 (4)	0.038 (4)	0.011 (3)	0.023 (3)	0.014 (3)
C4	0.062 (4)	0.058 (4)	0.041 (4)	0.008 (3)	0.026 (3)	0.014 (3)
C5	0.049 (3)	0.042 (4)	0.031 (3)	0.005 (3)	0.013 (3)	0.015 (3)
C6	0.060 (4)	0.064 (5)	0.040 (4)	0.013 (4)	0.016 (3)	0.016 (4)
C7	0.063 (4)	0.069 (5)	0.057 (5)	0.022 (4)	0.023 (4)	0.025 (4)

Geometric parameters (\AA , $^\circ$)

N1—C2	1.340 (7)	C3—H3A	0.9300
N1—C6	1.352 (8)	C4—C5	1.389 (8)
N1—H1A	0.8600	C4—H4A	0.9300
I1—Br1	2.6836 (10)	C5—C6	1.334 (8)
I1—Br2	2.7119 (10)	C5—C7	1.496 (8)
N2—C2	1.330 (7)	C6—H6A	0.9300
N2—H2A	0.8600	C7—H7A	0.9600
N2—H2B	0.8600	C7—H7B	0.9600
C2—C3	1.402 (8)	C7—H7C	0.9600
C3—C4	1.348 (8)		
C2—N1—C6	123.5 (5)	C3—C4—H4A	118.0
C2—N1—H1A	118.3	C5—C4—H4A	118.0
C6—N1—H1A	118.3	C6—C5—C4	115.2 (6)
Br1—I1—Br2	177.67 (2)	C6—C5—C7	121.3 (6)
C2—N2—H2A	120.0	C4—C5—C7	123.5 (5)
C2—N2—H2B	120.0	C5—C6—N1	122.1 (6)
H2A—N2—H2B	120.0	C5—C6—H6A	118.9
N2—C2—N1	120.1 (6)	N1—C6—H6A	118.9
N2—C2—C3	123.6 (6)	C5—C7—H7A	109.5
N1—C2—C3	116.3 (6)	C5—C7—H7B	109.5
C4—C3—C2	118.9 (6)	H7A—C7—H7B	109.5
C4—C3—H3A	120.5	C5—C7—H7C	109.5
C2—C3—H3A	120.5	H7A—C7—H7C	109.5

C3—C4—C5	123.9 (6)	H7B—C7—H7C	109.5
C6—N1—C2—N2	−179.2 (6)	C3—C4—C5—C6	0.0 (10)
C6—N1—C2—C3	2.4 (9)	C3—C4—C5—C7	−179.7 (6)
N2—C2—C3—C4	−179.7 (6)	C4—C5—C6—N1	1.0 (10)
N1—C2—C3—C4	−1.4 (9)	C7—C5—C6—N1	−179.3 (6)
C2—C3—C4—C5	0.3 (10)	C2—N1—C6—C5	−2.3 (10)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 <i>A</i> \cdots Br2	0.86	2.73	3.499 (5)	150
N2—H2 <i>B</i> \cdots Br1 ⁱ	0.86	2.70	3.545 (6)	168

Symmetry code: (i) $-x+1, -y, -z+1$.